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**Structural variability in Solutions, Crystals and
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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

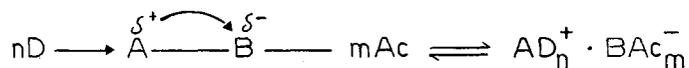
Chimica. — *Structural variability in Solutions, Crystals and Interfaces.* Nota di VIKTOR GUTMANN (*), presentata (**) dal Socio G. SARTORI.

RIASSUNTO. — Le regole di variazione della lunghezza di legame vengono applicate alle variazioni strutturali dei soluti nei solventi, dei solventi all'atto dell'introduzione dei soluti e alle conseguenze strutturali dei difetti puntiformi in cristalli reali.

Finalmente viene dimostrata la loro applicabilità ai fenomeni interfacciali.

I. STRUCTURAL VARIABILITY OF SOLUTES

Ionization of a covalent substrate A — B is due to both the donor and the acceptor functions of the solvent. By each of them the bond A — B is increased in polarity (push-pull effect) with ultimate formation of ions, which are stabilized by solvation:



For a given substrate A — B the equilibrium constant is greater the higher both the donor and the acceptor number of the solvent. Ionic reactions are best performed in a strongly amphoteric solvent (high DN and high AN), as both cations and anions are stabilized by solvation. Association of solvent molecules in the liquid state is also favored by high DN and high AN [1, 2].

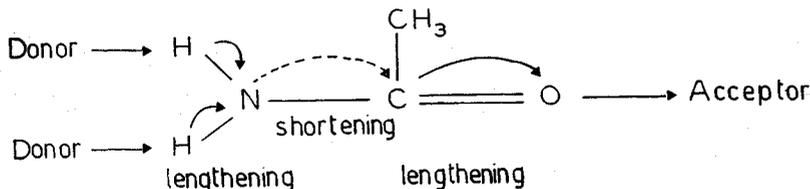
Highly reactive anions are produced in a solvent of high DN and of low AN, whereas reactive cations may be produced in a solvent of low DN and of high AN [2]. For an anionoid species of high nucleophilic property a solvent must have a "suitable" DN and an AN as low as possible. For a cationoid structure of high electrophilic property a solvent must have a moderately high AN but a DN as low as possible [1, 2]. An S_{N1} reaction is favored by both high DN and high AN, while an S_{N2} reaction is favored by low AN [1, 3].

Solvent effects on conformational changes have been established for acetamide, when donor attack takes place at the N—H atoms and acceptor attack at the oxygen atom of the C=O group [4]. The N—H bonds and the C=O bonds are lengthened increasingly both by increase in solvent donor

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number and by increase in solvent acceptor number. All of these effects lead to shortening of the C—N bond. In solvents of low acceptor number and of a donor number up to 20 one proton NMR signal is found, because of the free rotability of the C—N bond. However, in solvents of higher donor number two H—NMR signals are found, which indicate loss of free rotability of the C—N-bond due to induced double bond character.



2. STRUCTURAL VARIABILITY OF SOLVENTS

It is not only the solute structure that is modified but also the solvent is modified by the solute. The structural changes are at least in principle extending throughout the liquid phase and they are reflected in the structure and properties of the phase boundary [5]. In the inner hydration sphere of a metal ion the intramolecular O—H-bonds are longer (first bond length variation rule) and hence the acidic properties of the hydrogen atoms greater than in an undisturbed H₂O molecule. This leads to strong hydrogen bonding with the second hydration sphere. The electron drift from the oxygen atoms of the second sphere water molecules lengthens the adjacent O—H bonds and shortens the metal ion-inner sphere bond [5]. Formation of further hydration spheres involves cooperative electron effects in the same direction. With increasing distance from the metal ion the following effects are found: increasing O—O distances, decreasing H-bond energies, decreasing symmetry of H-bonds and decreasing linearity of H-bonds [1, 5]. Thus, there are structural gradients within microscopic areas of a liquid phase. In a solvent mixture preferential solvation by the more strongly solvating solvent component leads even to gradients in analytical composition within microscopic regions [7]. Solute-solute interactions are also mediated by the water molecules so that structural features are developed and maintained by collective actions [6]. It is therefore extremely unlikely to find two solvent molecules within a liquid phase in precisely the same state.

3. STRUCTURAL VARIABILITY IN REAL CRYSTALS

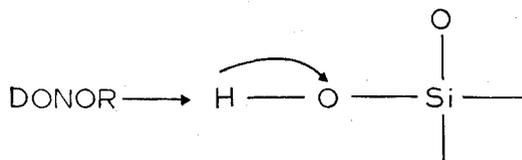
This model is applicable to the solid state, where structural inhomogeneities due to so-called "defects" have been disclosed [7]. It has been shown that a point defect is actually a center which is modified by the lattice and modifying an appreciable number of building units in its surroundings [8].

It has therefore been suggested to consider it an "SMM-center" (structure modified and modifying center). This term expresses the mutual interdependencies between the units, which are not equal, as may be assumed according to the model of the "ideal crystal" which, as is well-known, would be incapable of existence. Each point defect (SMM-center) is under stress and it exerts a strain on its environment. The far-reaching effects produced by a point defect are in principle continuous. The greater the distance of a building unit from a point defect (SMM-center) the smaller is its influence on the former. Such hardly distributed regions are important in separating the strongly "disturbed" regions from one another. These "separating" regions contribute mostly to the statistical information obtainable for example by X-ray diffraction analysis.

Point defects (SMM-centers) are known to migrate by exchanging places with building units [9]. The driving forces for such positional changes are gradients in chemical potential, which are structurally represented by structural inhomogeneities. It is, however, important to note that by any migration the overall pattern is not lost, so that fluctuations from equilibrium conditions are continuously taking place. They involve both drastic atomic rearrangements in small volumes and small rearrangements distributed over a large volume [10]. The regularities by which the interactions occur provide stationary patterns of inhomogeneities by which the properties are maintained [8].

4. STRUCTURAL VARIABILITY AT INTERFACES

The application of the donor-acceptor concept may also be of considerable value to structural considerations at interfaces. A crystal surface may be considered as an area of lattice distortion [11]. The lack of interactions in one dimension implies a lattice contraction in the surface area [12], which has been studied notably by the LEED-technique. For example, for the upper layer of a silver (110) plane a real contraction of 7% has been found [12, 13]. Such effects may be compensated or even overcompensated by adsorption. The stronger the adsorption, the greater is the lengthening of surface bonds (first bond length variation rule). For example the O—H bond lengthening on an aerosile surface has been found greater, the higher the donor number of the adsorbate attacking the surface hydrogen atoms [14].



Since adsorption leads to increasing bond distances within the surface area, desorption will lead to a corresponding decrease in bond distances. A

surface is contracted by adsorption and expanded by desorption and hence the surface is not rigid but rather distortable.

Surface atoms have been shown to control all other building units of the crystal and to respond to the interactions within the crystal [8]. Due to the displacement reactions taking place within the crystal, the surface must be subjected to related fluctuations. The surface contains the information of structure and dynamics of the whole phase in an integrated two-dimensional form. Each point of the surface contains information of the system as seen from the point under consideration, and hence fluctuations in the bulk are expected to be represented in a two-dimensional way in the surface [8].

5. CONCLUSIONS

The most remarkable aspects are the interdependencies of structural features of all parts of the system. The description by the bond length variation rules is virtually independent of the interpretation of the bonding forces. Changes due to molecular environment are correlated with differences in thermodynamic and kinetic parameters as well as with the empirical parameters which have been introduced, namely the donor number and the acceptor number. In this way it is possible to choose a suitable solvent for a desired reaction. The consideration of far-reaching effects provides an understanding of the properties of solutions, of real crystals, of interactions at interfaces and—as has been indicated elsewhere [1, 7]—of biochemical phenomena.

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